

## CHAPTER 18

### *Molecules and Radiation*

#### SECTION 18.1

18.1 A photon of frequency  $\nu = 10 \text{ GHz} = 10^{10} \text{ Hz}$  has an energy

$$E = h\nu = (6.626 \times 10^{-34} \text{ J Hz}^{-1}) (10^{10} \text{ Hz}) = 6.626 \times 10^{-24} \text{ J} .$$

A mole of these photons has an energy  $N_A$  times larger, or a molar energy

$$\bar{E} = N_A E = (6.626 \times 10^{-24} \text{ J}) (6.022 \times 10^{23} \text{ mol}^{-1}) = 4.0 \text{ J mol}^{-1} .$$

Thus, a microwave source radiating 4 J onto a  $1 \text{ cm}^2$  area each second (a flux of  $4 \text{ W cm}^{-2}$ ) spews a mole of photons onto that illuminated area each second. (Note that the wavelength of these photons is  $\lambda = c/\nu \cong 3 \text{ cm}$ . Microwaves move through waveguides that have linear dimensions on the order of their wavelength so that the  $1 \text{ cm}^2$  illumination area is the right order of magnitude for the cross-sectional area of a 10 GHz waveguide.)

18.2 A photon of wavelength  $\lambda = 555 \text{ nm} = 5.55 \times 10^{-7} \text{ m}$  has an energy

$$E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J Hz}^{-1}) (2.998 \times 10^8 \text{ m s}^{-1})}{5.55 \times 10^{-7} \text{ m}} = 3.58 \times 10^{-19} \text{ J} .$$

If we multiply the radiation intensity,  $2 \times 10^{-16} \text{ W cm}^{-2}$ , by the illuminated area  $A$  and divide by this photon energy, we have the number of photons striking  $A$  per second. What you choose for  $A$  depends on how you measure your eye's pupil, but since we are considering a minimum detectable light flux, we want a pupil area that is as large as physiologically possible, since our environment is obviously pretty dark! An area  $\sim 0.3 \text{ cm}^2$  is in the right range, and with this  $A$ , we find that about 170 photons strike one eye per second.

- 18.3 A wavenumber of  $1000 \text{ cm}^{-1}$  corresponds to a wavelength that is the reciprocal of this number:  $\lambda = (1/1000) \text{ cm} = 10^{-5} \text{ m}$ . This photon's energy is  $E = hc/\lambda = 1.98 \times 10^{-20} \text{ J}$ . A 10 MW power delivers  $10^7 \text{ J s}^{-1}$ , but if the laser is on for only the duration of a 5 ns pulse, the total energy in the pulse is  $(10^7 \text{ J s}^{-1})(5 \times 10^{-9} \text{ s}) = 0.05 \text{ J} = 50 \text{ mJ}$ . Dividing this by the energy per photon tells us that each pulse contains  $(0.05 \text{ J})/(1.98 \times 10^{-20} \text{ J photon}^{-1}) = 2.52 \times 10^{18}$  photons. If the pulses repeat at a 10 Hz rate, each second delivers energy at the average rate  $(50 \text{ mJ pulse}^{-1}) \times (10 \text{ pulses s}^{-1}) = 0.50 \text{ J s}^{-1} = 0.50 \text{ W}$ . If these pulses are focused to a  $1 \text{ mm}^2 = 10^{-6} \text{ m}^2$  spot, the fluence is the pulse energy divided by the area:  $50 \text{ mJ}/10^{-6} \text{ m}^2 = 50 \text{ kJ m}^{-2}$ .

## SECTION 18.2

- 18.4 Equation (18.8) reads

$$\rho(\nu; T) d\nu = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{h\nu/k_B T} - 1} d\nu .$$

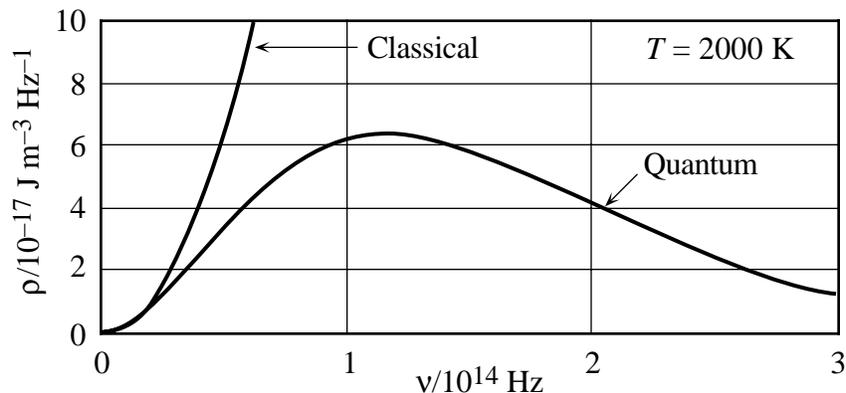
The classical limit is  $h\nu \ll k_B T$  (since this means the characteristic quantum of energy,  $h\nu$ , is much smaller than the characteristic microscopic thermal energy  $k_B T$  so that quantized energy differences blend into a continuum of energy, as expected classically), and in this limit, we can expand the exponential in the denominator of the Eq. (18.8):

$$e^{h\nu/k_B T} - 1 \cong \left( 1 + \frac{h\nu}{k_B T} + \dots \right) - 1 = \frac{h\nu}{k_B T} ,$$

and Eq. (18.8) becomes

$$\rho(\nu; T) d\nu \cong \frac{8\pi h\nu^3}{c^3} \frac{k_B T}{h\nu} d\nu = \frac{8\pi k_B T}{c^3} \nu^2 d\nu .$$

The failure of the classical expression to reproduce observed blackbody emission was called the “ultraviolet catastrophe” at the time, since the disagreement between this expression and observation was most noticeable at high frequencies, i.e., in the ultraviolet region and beyond, where the classical expression diverges. This is shown in the figure at the top of the next page, which plots  $\rho$  for both the quantum theory and the classical theory for  $T = 2000 \text{ K}$ .



- 18.5 The blackbody radiation intensity is  $I = \sigma T^4$  (see page 670 in the text) where  $\sigma$  is the Stephan–Boltzmann constant,  $5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$ . For  $T = 1500 \text{ K}$ ,  $I = 2.87 \times 10^5 \text{ W m}^{-2}$ , and if the blackbody glowbar area is  $10 \text{ cm}^2 = 10^{-3} \text{ m}^2$ , we must supply it with energy at the rate  $(2.87 \times 10^5 \text{ W m}^{-2}) \times (10^{-3} \text{ m}^2) = 287 \text{ W}$ . This is a typical power requirement—something on the order of 100 W—for most small blackbody radiators, from glowbars to incandescent light-bulbs.
- 18.6 The radiation energy density per unit frequency interval at frequency  $\nu_0$  and temperature  $T$ ,  $\rho(\nu_0; T)$ , is, according to Eq. (18.8),

$$\rho(\nu_0; T) = \frac{8\pi h \nu_0^3}{c^3} \frac{1}{e^{h\nu_0/k_B T} - 1} = 7.59 \times 10^{-19} \text{ J m}^{-3} \text{ Hz}^{-1}$$

for  $\nu_0 = 4.738 \times 10^{14} \text{ Hz}$  and  $T = 2000 \text{ K}$ . With a frequency interval  $\Delta\nu = 3 \times 10^8 \text{ Hz}$ , the energy density is  $\rho(\nu_0; T)\Delta\nu = 2.28 \times 10^{-10} \text{ J m}^{-3}$ . The radiation intensity is  $c$  times larger than this:  $\rho\Delta\nu c = 6.83 \times 10^{-2} \text{ W m}^{-2}$ . A sphere with a radius  $R = 1 \text{ m}$  has an area  $A = 4\pi R^2 = 12.6 \text{ m}^2$ , and one photon of frequency  $\nu_0$  has an energy  $E = h\nu_0 = 3.14 \times 10^{-19} \text{ J}$ . Thus, the number of photons illuminating the interior of a 1 m radius sphere with our blackbody at its center is

$$\frac{(6.83 \times 10^{-2} \text{ W m}^{-2})(12.6 \text{ m}^2)}{3.14 \times 10^{-19} \text{ J photon}^{-1}} = 2.73 \times 10^{18} \text{ photon s}^{-1} .$$

A spot with a 1 mm radius has an area  $a = \pi r^2 = 3.14 \times 10^{-6} \text{ m}^2$ , and the fraction of all the photons illuminating a spot this big inside the  $R = 1 \text{ m}$  sphere is

$$\frac{a}{A} = \frac{\pi r^2}{4\pi R^2} = \frac{3.14 \times 10^{-6} \text{ m}^2}{12.6 \text{ m}^2} = 2.5 \times 10^{-7}$$

so that only  $(2.5 \times 10^{-7}) \times (2.73 \times 10^{18} \text{ photons s}^{-1}) = 6.8 \times 10^{11}$  black-body photons strike the 1 mm radius spot per second *in a frequency interval  $\Delta\nu$  centered around this  $\nu_0$* .

- 18.7 Continuing from the previous problem (and using its notation), we now ask for the temperature  $T$  of a blackbody that could produce  $3.2 \times 10^{15}$  photon  $\text{s}^{-1}$  at the spot of area  $a$ . Thus, we seek  $T$  such that

$$\rho(\nu_0; T)\Delta\nu \frac{ac}{h\nu_0} = \frac{8\pi h\nu_0^3}{c^3} \frac{\Delta\nu}{e^{h\nu_0/k_B T} - 1} \frac{ac}{h\nu_0} = 3.2 \times 10^{15} \text{ photon s}^{-1} .$$

This expression can be solved for  $T$  or the value for  $T$  can be found iteratively using a spreadsheet program or a calculator. We find  $T = 7656 \text{ K}$ .

- 18.8 The phenomenology of resonance radiation can be understood and explained in these terms. First, the directed beam of yellow light produced from Na atom emission must come from a transition in the atom in which the initial excited state emits a photon and ends in the atomic *ground state*. This must be the case because the vaporized Na in the adjacent evacuated tube consists of ground state atoms, not excited atoms (or otherwise we would see a noticeable yellow glow from unilluminated Na(*g*) alone, and we do not). Now consider what happens to the yellow light when it is absorbed by a Na(*g*) atom just inside the evacuated tube's wall: the ground state Na becomes an excited state Na once it absorbs the yellow photon, but only a few ns later, this excited atom re-emits the yellow photon, *randomly in any direction*. (We see the yellow glow with the same intensity if we look at the tube from any direction.) As the Na(*g*) density is increased through an increase in pressure, the number of possible absorbing Na atoms near the illuminated wall of the tube increases. The Na gas becomes increasingly more opaque to the illuminating yellow light. At very high pressures, all this light is absorbed by Na atoms perhaps only a  $\mu\text{m}$  inside the tube. The absorbed light is emitted in all directions from this spot. In contrast, low pressures allow the illuminating light to penetrate more deeply into the gas. The excitation gradually decreases with distance into the gas, as the illuminating beam is slowly attenuated, and the excited atoms fluoresce along the path of the illumination, forming a cone of fluorescence.

### SECTION 18.3

18.9 The transition dipole moment expression for the system of Example 18.2 with the coordinate origin shift suggested in the problem is

$$\begin{aligned} p_{12} &= \int \psi_1 \hat{p} \psi_2 dx = -\frac{2e}{L} \int_0^L \sin\left(\frac{\pi x}{L}\right) \left(x - \frac{L}{2}\right) \sin\left(\frac{2\pi x}{L}\right) dx \\ &= -\frac{2e}{L} \int_0^L \sin\left(\frac{\pi x}{L}\right) x \sin\left(\frac{2\pi x}{L}\right) dx + e \int_0^L \sin\left(\frac{\pi x}{L}\right) \sin\left(\frac{2\pi x}{L}\right) dx . \end{aligned}$$

Note that the first term in the final expression is identical to that in Example 18.2 and that the second term is zero due to the orthogonality of  $\psi_1$  and  $\psi_2$ . Thus, the transition dipole moment is independent of coordinate origin.

18.10 As in Example 18.2, we start with the transition dipole moment. Here we consider the  $n = 3$  to  $n = 2$  transition:

$$\begin{aligned} p_{23} &= \int \psi_2 \hat{p} \psi_3 dx = -\frac{2e}{L} \int_0^L \sin\left(\frac{2\pi x}{L}\right) x \sin\left(\frac{3\pi x}{L}\right) dx \\ &= -\frac{2e}{L} \frac{L^2}{\pi^2} \int_0^\pi \sin(2y) y \sin(3y) dx = \left(-\frac{2e}{L} \frac{L^2}{\pi^2}\right) \left(-\frac{24}{25}\right) \\ &= \frac{48eL}{25\pi^2} . \end{aligned}$$

Next, we calculate the transition frequency,  $\nu_{23}$ :

$$\nu_{23} = \frac{E_3 - E_2}{h} = \frac{\pi^2 \hbar^2}{2m_e h L^2} (3^2 - 2^2) = \frac{5\pi^2 \hbar^2}{2m_e h L^2} .$$

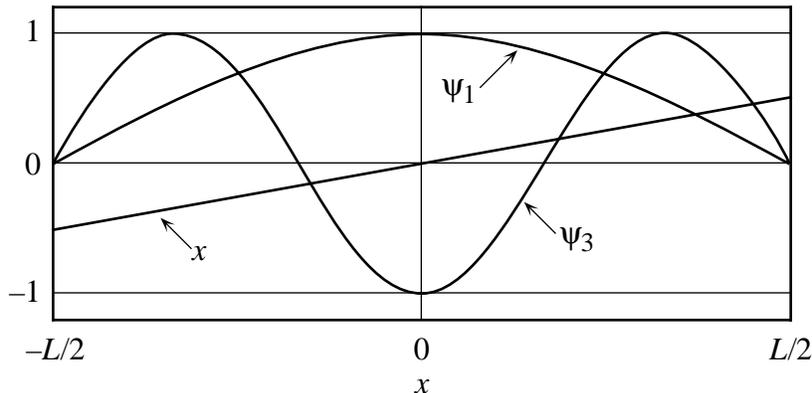
Next, we calculate  $B_{23}$  from Eq. (18.21):

$$B_{23} = \frac{p_{23}^2}{6\epsilon_0 \hbar^2} = \frac{48^2 e^2 L^2}{6\epsilon_0 \hbar^2 25^2 \pi^4} = \frac{384 e^2 L^2}{625 \pi^4 \epsilon_0 \hbar^2} .$$

Finally, we calculate the transition rate itself:

$$A_{23} = \frac{8\pi h\nu_{23}^3}{c^3} B_{23} = \frac{24e^2 h^2}{5c^3 m_e^3 \pi \epsilon_0 L^4}.$$

A radiative transition will not have a high probability if the transition dipole moment is zero. For the  $n = 3$  to  $n = 1$  transition, the three functions that are multiplied to form the integrand of the transition moment integral,  $\psi_1 x \psi_3 = \sin(\pi x/L) x \sin(3\pi x/L)$ , are shown in the graph below with the  $x$  axis origin shifted to the center of the 1-D box. (The previous problem proved that the transition moment is independent of the coordinate origin.)



We can see from the graphs that  $\psi_1$  and  $\psi_3$  are symmetric about the origin, but the factor of  $x$  from the dipole moment operator is not. Since the integration range is symmetric about the origin (i.e., from  $-L/2$  to  $L/2$ ), the integral must equal zero due to the symmetry of the factor of  $x$  in the integrand. Thus, the transition moment vanishes, and the  $n = 3$  to  $n = 1$  transition is not allowed.

18.11 The H atom 1s and 2p<sub>z</sub> wavefunctions are listed in Table 12.4:

$$\psi_{1s} = \frac{1}{\sqrt{\pi}} \frac{1}{a_0^{3/2}} e^{-r/a_0} \quad \text{and} \quad \psi_{2p_z} = \frac{1}{\sqrt{\pi}} \frac{1}{a_0^{3/2}} e^{-r/2a_0} \frac{1}{4\sqrt{2}} \frac{r}{a_0} \cos \theta.$$

A transition between these two states is possible only if the transition dipole moment has at least one nonzero component value. The three transition moment integrals, one for each polarization direction, are

$$\begin{aligned}
p_{x,12} &= -e \int \psi_{1s} x \psi_{2p_z} d\tau \\
p_{y,12} &= -e \int \psi_{1s} y \psi_{2p_z} d\tau \\
p_{z,12} &= -e \int \psi_{1s} z \psi_{2p_z} d\tau .
\end{aligned}$$

While we will evaluate the only one of these integrals that is nonzero later in this problem using spherical polar coordinates, it is helpful first to consider them in Cartesian coordinates (i.e., as triple integrals, each from  $-\infty$  to  $\infty$ , over  $x$ ,  $y$ , and  $z$ ). The  $\psi_{1s}$  function is symmetric about the coordinate origin for each polarization direction:  $\psi_{1s}(x, y, z) = \psi_{1s}(-x, y, z) = \psi_{1s}(x, -y, z) = \psi_{1s}(x, y, -z)$ , and the  $\psi_{2p_z}$  function is symmetric about the origin in the  $x$  and  $y$  directions, but in the  $z$  direction, it is antisymmetric:  $\psi_{2p_z}(x, y, z) = -\psi_{2p_z}(x, y, -z)$ . Now consider the integration over  $x$  in the expression for  $p_{x,12}$ . Both wavefunctions are symmetric, but the factor of  $x$  from the dipole moment operator makes the full integrand antisymmetric. The integral over  $x$  from  $-\infty$  to  $0$  is exactly the negative of that from  $0$  to  $\infty$ . Thus,  $p_{x,12}$  vanishes. The same argument holds for  $p_{y,12}$  when integrated over  $y$  (or for either when integrated over  $z$ ). For the  $p_{z,12}$  integral, however, the factor of  $z$  in the integrand makes the integral symmetric with respect to  $z$  ( $z$  times  $\psi_{2p_z}$  is symmetric, and  $\psi_{1s}$  already was). It is also symmetric with respect to  $x$  and  $y$  and therefore must be nonzero. Thus, the only nonzero integral evaluates to (with the help of the first integral given in the problem)

$$\begin{aligned}
p_{z,12} &= -e \int \psi_{1s} z \psi_{2p_z} d\tau = -e \int \psi_{1s} r \cos \theta \psi_{2p_z} d\tau \\
&= -\frac{e}{4\pi a_0^3 \sqrt{2}} \int_{r=0}^{\infty} \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} e^{-3r/2a_0} \frac{r^2}{a_0} \cos^2 \theta r^2 \sin \theta dr d\theta d\phi \\
&= -\frac{2\pi e}{4\pi a_0^4 \sqrt{2}} \int_{r=0}^{\infty} \int_{\theta=0}^{\pi} e^{-3r/2a_0} r^4 \cos^2 \theta \sin \theta dr d\theta \\
&= -\frac{e}{3a_0^4 \sqrt{2}} \int_0^{\infty} r^4 e^{-3r/2a_0} dr .
\end{aligned}$$

If we define  $x = 3r/2a_0$ , we can complete the final integral:

$$\begin{aligned} p_{z,12} &= -\frac{e}{3a_0^4\sqrt{2}} \int_0^\infty r^4 e^{-3r/2a_0} dr = -\frac{e}{3a_0^4\sqrt{2}} \left(\frac{2a_0}{3}\right)^5 \int_0^\infty x^4 e^{-x} dx \\ &= -\frac{ea_0}{\sqrt{2}} \frac{2^5}{3^6} 24 = -\frac{256}{243\sqrt{2}} ea_0 = -6.315 \times 10^{-30} \text{ C m} . \end{aligned}$$

18.12 Given the transition dipole moment integral for the  $1s$  to  $2p_z$  transition in atomic hydrogen from the previous problem, we can calculate the Einstein spontaneous emission coefficient  $A_{21}$  if we first calculate the Einstein  $B_{12}$  coefficient:

$$B_{12} = \frac{|p_{12}|^2}{6\epsilon_0 \hbar^2} = \frac{(6.315 \times 10^{-30} \text{ C m})^2}{6\epsilon_0 \hbar^2} = 6.751 \times 10^{19} \text{ m}^3 \text{ J}^{-1} \text{ s}^{-2} .$$

Given  $B_{12}$ , we can calculate  $A_{21}$  through the expression

$$A_{21} = \frac{8\pi h \nu_{12}^3}{c^3} B_{12} .$$

We can easily find the transition frequency  $\nu_{12}$  if we recall that the  $n = 2$  state's energy in H atom is above the  $n = 1$  ground state energy by an amount equal to three-fourths the atom's ionization energy (see the Summary to Chapter 12 and the pattern of energy levels for H atom shown on page 441 in the text):

$$\nu_{12} = \frac{\Delta E_{12}}{h} = \frac{3}{4} \frac{2.179 \times 10^{-18} \text{ J}}{h} = 2.466 \times 10^{15} \text{ Hz} .$$

Thus,  $A_{21}$  is

$$A_{21} = \frac{8\pi h \nu_{12}^3}{c^3} B_{12} = 6.258 \times 10^8 \text{ s}^{-1} .$$

This is three-fourths the value that is tabulated as “the average ... for the  $n = 2$  to  $n = 1$  transition” for two reasons: there are four essentially degenerate states with  $n = 2$  (i.e.,  $2s$ ,  $2p_x$ ,  $2p_y$ , and  $2p_z$ ), only one of which ( $2p_z$ ) can emit by  $z$ -

polarized light (there's the denominator of four in the expression "three-fourths the value that is tabulated"), but there is nothing special about the  $z$  direction—it is only one of three possible polarizations (there's the numerator of three). Put another way, of the four states with  $n = 2$ , three of them can readily radiate to  $n = 1$ . The  $2s$  to  $1s$  transition is not allowed by our electric dipole transition expressions for any polarization.

- 18.13 First, we note that the fluorescence intensity is a direct measure of the number of excited atoms at any time:  $I(t) \propto N_2(t)$ , in the notation of Eq. (18.22). Consequently, we can write

$$\frac{I(t)}{I(t=0)} = \frac{N_2(t)}{N_2^o} = e^{-t/\tau_{\text{rad}}}.$$

The graph given with the problem shows that the fluorescence intensity falls to half its initial value about 1 ns after the initial excitation. Thus, the expression above becomes

$$\frac{I(1 \text{ ns})}{I(t=0)} = \frac{N_2(1 \text{ ns})}{N_2^o} = 0.5 = e^{-10^{-9} \text{ s}/\tau_{\text{rad}}},$$

and we can solve this expression for  $\tau_{\text{rad}}$ , finding  $\tau_{\text{rad}} = 1.4 \times 10^{-9} \text{ s}$ . The spontaneous emission coefficient is just the reciprocal of  $\tau_{\text{rad}}$ :  $A_{21} = 1/\tau_{\text{rad}} = 7.0 \times 10^8 \text{ s}^{-1}$ .

- 18.14 If  $A_{21} = 2.87 \times 10^{-15} \text{ s}^{-1}$ , then  $\tau_{\text{rad}} = 1/A_{21} = 3.48 \times 10^{14} \text{ s} \cong 1.1 \times 10^7 \text{ yr}$ . If the characteristic time for this light to be emitted is on the order of ten million years, this radiative transition must be an extremely unlikely one! There is plenty of time for collisions to excite ground-state H atoms from the  $F = 0$  to the excited  $F = 1$  level (and to relax  $F = 1$  back to  $F = 0$ ), even though any *one* collision happens to have a very small probability of changing the  $F$  state. (In less dense interstellar regions, collisions occur as infrequently as once per year.) Since the emission probability is very small (in part because the photon energy and frequency is very small—see page 579 in the text—but also because this type of transition is forbidden by the electric dipole transition rules we have discussed in this chapter), so too must be the absorption probability. This means that the photon, once emitted, is very unlikely to be reabsorbed by a ground-state H atom on its journey to Earth.

- 18.15 Given  $p_{12} = 1.6 \times 10^{-29}$  C m, we can find the radiative lifetime from the expression

$$\tau_{\text{rad}} = \frac{1}{A_{21}} = \frac{c^3}{8\pi h \nu_{12}^3} \frac{6\epsilon_0 \hbar^2}{p_{12}^2}$$

once we know the transition frequency,  $\nu_{12}$ . If the transition energy  $\Delta E$  is expressed in wavenumber units, we can calculate  $\nu_{12}$  from

$$\nu_{12}/\text{Hz} = (\Delta E/\text{cm}^{-1}) \times (c/\text{m s}^{-1}) \times (100 \text{ cm m}^{-1}).$$

We thus construct the table below:

Transition	$\Delta E/\text{cm}^{-1}$	$\nu_{12}/\text{Hz}$	$\tau_{\text{rad}}$
(a) X ray	$2 \times 10^5$	$6 \times 10^{12}$	$1.7 \times 10^{-11}$ s = 17 ps
(b) Visible	$2 \times 10^4$	$6 \times 10^{14}$	$1.7 \times 10^{-8}$ s = 17 ns
(c) Infrared	$10^3$	$3 \times 10^{13}$	$1.4 \times 10^{-4}$ s = 14 ms
(d) Microwave	1	$3 \times 10^{10}$	$1.4 \times 10^5$ s = 38 hr

The key result here is that a frequency change on the order of  $10^5$  changes the radiative lifetime by a factor on the order of  $(10^5)^3 = 10^{15}$ .

- 18.16 Radiation of wavelength  $\lambda = 600$  nm has a frequency  $\nu = c/\lambda = 5 \times 10^{14}$  Hz. Thus, in  $10$  fs =  $10^{-14}$  s, this radiation undergoes  $(10^{-14} \text{ s}) \times (5 \times 10^{14} \text{ cycles s}^{-1}) = 5$  cycles. Page 678 in the text shows that  $\Delta E \tau \cong \hbar/2$  or  $\Delta \nu \tau \cong 1/4\pi$ . If  $\tau \cong 10^{-14}$  s, then  $\Delta \nu \cong 1/4\pi \tau = 8 \times 10^{12}$  Hz so that  $\Delta \nu/\nu = 0.016$ . The frequency precision of a 10 fs light pulse cannot be better than about 1% for light in the visible frequency range.
- 18.17 The Cd ground-state configuration,  $5s^2$ , has even parity, since each electron (outside the closed, inner shells) has  $l = 0$ . Each excited state based on the  $5s^1 5p^1$  configuration has *odd* parity, since the s electron has even parity but the p electron ( $l = 1$ ) has odd parity and we follow the rule that  $\text{odd} \times \text{even} = \text{odd}$ . Thus, we can construct the table at the top of the next page listing the transitions to the ground state that are allowed under normal  $L-S$  selection rules and those allowed under selection rules based on  $J$  only.

	$5s^2\ ^1S_0$	$5s^15p^1\ ^3P_0$	$5s^15p^1\ ^3P_1$	$5s^15p^1\ ^3P_2$	$5s^15p^1\ ^1P_1$
Parity:	even	odd	odd	odd	odd
$L$ - $S$ rules:		no	no	no	yes
$J$ rules:		no	yes	no	yes

Under  $L$ - $S$  rules, the triplet excited states cannot radiate to the singlet ground state, but the singlet excited state can, since  $L$  changes by 1, as does  $J$ . Under the  $J$  rules, emission from  $^3P_0$  to the ground state is not allowed because  $J = 0$  to  $J = 0$  transitions are forbidden. The  $^3P_2$  state cannot emit because  $J$  cannot change by 2.

- 18.18 The statement “transitions that do not change atomic configuration are forbidden” is a valid expression of Laporte’s rule. Any one configuration has a unique parity no matter what state or states are derived from it, and Laporte’s rule states that parity must change in a dipole-allowed transition. The converse, that all transitions that *do* change configuration *are* allowed, is false, however. (And finally, since the rule holds only for dipole-allowed transitions, it does not predict which transitions might be allowed—but improbable—by another radiative mechanism.)
- 18.19 The longest wavelength allowed transition of ground-state N is the  $2p^3\ ^4S_{3/2}^0 \rightarrow 2p^23s^1\ ^4P_{1/2}$  transition at  $83\ 285.5\ \text{cm}^{-1}$  (or 120.07 nm wavelength). The  $2p^3\ ^2P_{3/2}^0$  excited state cannot emit under  $L$ - $S$  selection rules; it has the same parity (odd) as all states lower in energy than it. The  $2p^23s\ ^4P_{5/2}$  state can emit to the  $2p^3\ ^4S_{3/2}^0$  ground state only; this is the only lower energy quartet state of a different parity.
- 18.20 The situation here is very similar to that of Cd in Problem 18.17. The ground state of Ba is  $6s^2\ ^1S_0$ , and the first excited state that can readily emit to this state is the  $6s^16p^1\ ^1P_1^0$  state.
- 18.21 The Tl ground state is  $6s^26p^1\ ^2P_{1/2}^0$ , and we seek an excited state that is radiatively connected to this one. We note that the state we seek must have even parity, and the only low-lying state with even parity is the  $6s^27s^1\ ^2S_{1/2}$  state at  $26\ 478\ \text{cm}^{-1}$ . This corresponds to a wavelength of 377.67 nm, which falls in the range accessible to your laser. Thus, you can do the experiment.
- 18.22 Table 13.3 lists the following states with the  $2s^12p^3$  configuration:  $2p^3\ ^3D^0$ ,  $2p^3\ ^5S^0$ , and  $2p^3\ ^3P^0$ . These are half the total, and we find all of them if we start in Table 13.2, which tells us that the  $p^3$  configuration alone generates  $^2P$ ,

$^2D$ , and  $^4S$  terms. We couple the single  $s$  electron in the  $2s^1 2p^3$  configuration to each of these three term symbols. A single  $s$  electron has  $l = 0$  so that  $L$  will not change (i.e., we still have only  $S$ ,  $P$ , and  $D$  terms), but this electron's spin can either add to or subtract from the total  $S$  of the  $p^3$  terms. Thus, the six terms symbols in all (and note that each is of odd parity) are  $^5S^o$ ,  $^3S^o$ ,  $^3D^o$ ,  $^1D^o$ ,  $^3P^o$ , and  $^1P^o$ . The ground state of  $C$  is  $2s^2 2p^2 \ ^3P$ , and this term can connect to any of the triplets (conserving spin multiplicity and changing parity) except those transitions that start and end with  $J = 0$ , which is not allowed.

- 18.23 The  $2p^1 \ ^2P_{1/2}^o$  excited state radiative lifetime, 1.6 ns, was calculated in Problem 18.12 in terms of the spontaneous emission rate. We noted there that this was the only state for which the transition dipole moment integral was nonzero, and we can express the same idea here in terms of selection rules. For the  $2s^1 \ ^2S_{1/2} \rightarrow 1s^1 \ ^2S_{1/2}$  transition, the parity does not change, and the rule that a state with  $L = 0$  cannot connect to another state with  $L = 0$  is violated. Thus, this is a forbidden transition with a very long radiative lifetime. The  $2s^1 \ ^2S_{1/2}$  state manages to radiatively relax through simultaneous *two photon emission*. This is analogous to the emission route used by the  $He \ 1s^1 2s^1 \ ^1S_0$  state mentioned on page 682 in the text.

## SECTION 18.4

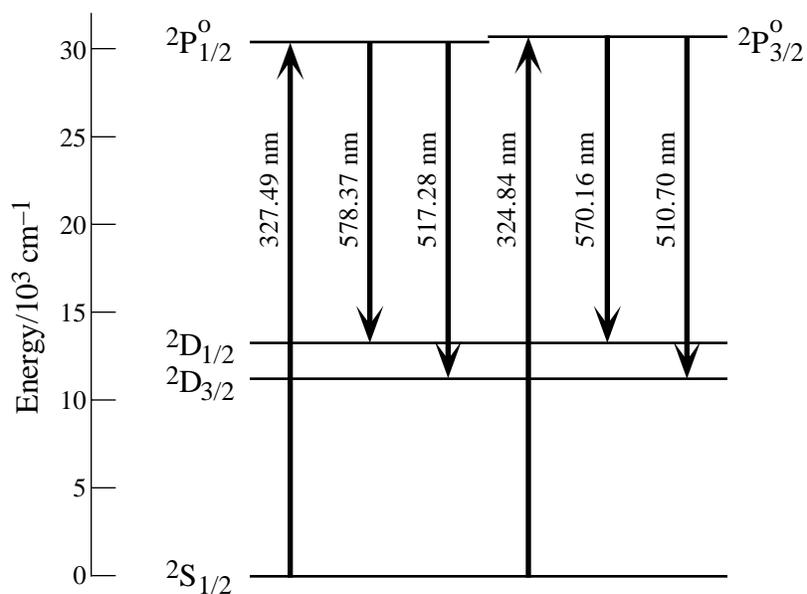
- 18.24 A wavelength of 148 nm corresponds to a photon frequency  $\nu = 2.03 \times 10^{15}$  Hz or a photon energy  $h\nu = 1.34 \times 10^{-18}$  J = 8.38 eV. Table 7.3 lists the ionization potential of  $Ca$  as 6.111 eV, which tells us that our 148 nm photon has photoionized  $Ca$ . The  $500 \text{ cm}^{-1}$  linewidth for this transition corresponds to an energy spread  $\Delta E \cong 1 \times 10^{-20}$  J or a frequency spread a factor of  $h$  smaller,  $\Delta\nu = 1.5 \times 10^{13}$  Hz. The excited state's lifetime is  $\tau = 1/4\pi\Delta\nu \cong 5 \times 10^{-15}$  s (see Problem 18.16), which is a typical value for an autoionizing state.
- 18.25 The lowest energy  $He^-$  electron configuration that can give a  $^4P$  term is the  $1s^1 2s^1 2p^1$  configuration: three unpaired spins coupled in a quartet fashion with the single  $p$  electron giving  $L = 1$ . The  $1s^1 2s^1$  states of  $He$  (with term symbols  $^1S_0$  and  $^3S_1$ ) cannot radiate (they are *metastable*—see page 681 in the text) and can be generated experimentally by electron bombardment of ground state  $1s^2 \ ^1S_0$   $He$ . Helium atoms in one of these states are poised to capture a third electron into the  $2p$  orbital and form the relatively long-lived  $^4P$  anion state.
- 18.26 A photon of wavelength  $\lambda = 300$  nm has a frequency  $\nu = c/\lambda = 1.0 \times 10^{15}$  Hz and an energy  $E = h\nu = 6.6 \times 10^{-19}$  J = 4.13 eV. If the  $F_2$  bond energy is

1.56 eV, the excess energy available to the dissociating atoms is  $4.13 \text{ eV} - 1.56 \text{ eV} = 2.57 \text{ eV}$ . If we wish to form the atoms with 2.00 eV excess energy, we need to irradiate  $\text{F}_2$  with a photon of energy  $E = 2.00 \text{ eV} + 1.56 \text{ eV} = 3.56 \text{ eV} = 5.70 \times 10^{-19} \text{ J}$ . Such a photon has a wavelength  $\lambda = hc/E = 348 \text{ nm}$ .

- 18.27 A photon of wavelength  $\lambda = 185 \text{ nm}$  has an energy  $E = hc/\lambda = 1.07 \times 10^{-18} \text{ J} = 6.70 \text{ eV}$ . If the ground-state dissociation energy of HBr is 3.75 eV, photodissociation with this 6.70 eV photon leaves  $6.70 \text{ eV} - 3.75 \text{ eV} = 2.95 \text{ eV}$  excess energy. Since the H-atom photofragment has this amount of kinetic energy, we can conclude that the Br-atom photofragment must be in its ground electronic state. Example 13.5 tells us that the first excited electronic state of Br lies  $3685 \text{ cm}^{-1} = 0.457 \text{ eV}$  above the ground state. If HBr photodissociation left the Br atom in this state, the kinetic energy of the H-atom photofragment would have to be 0.457 eV less than the excess energy, or about 2.49 eV. If we photodissociate HBr with a 248 nm photon (which has  $E = 5.00 \text{ eV}$ ), we have  $5.00 \text{ eV} - 3.75 \text{ eV} = 1.25 \text{ eV}$  excess energy. Again, this is the observed H-atom photofragment kinetic energy, and we can conclude that the Br atom is formed in its ground electronic state at this wavelength as well as at 185 nm.

## GENERAL PROBLEMS

- 18.28 The idea here is to use one laser to populate an excited electronic state that has a large transition probability from the ground state and then to use a second laser to *stimulate* emission *from* this excited state to another state that is above the ground state but below the initial excited state in energy. Both transitions must be individually allowed transitions, and for Cu, the energy level diagram at the top of the next page shows how this can be done with the lasers described in the problem. The UV laser (the one that can be tuned around 325 nm in this problem) is called the “pump” laser in this kind of experiment. It is set to either 327.49 nm (to pump the  $^2\text{S}_{1/2} \rightarrow ^2\text{P}_{1/2}^o$  transition) or to 324.84 nm (to pump the  $^2\text{S}_{1/2} \rightarrow ^2\text{P}_{3/2}^o$  transition). Both of these transitions are fully allowed. The second laser is called the “dump” laser; it dumps excited state population produced by the first laser into a lower-lying level through a stimulated emission process. If this laser is tuned to 578.37 nm while the first is at 327.49 nm, the diagram shows that we effect the transition from the  $^2\text{S}_{1/2}$  ground state to the  $^2\text{D}_{1/2}$  excited state by way of the  $^2\text{P}_{1/2}^o$  state. Similar arguments hold for production of the  $^2\text{D}_{3/2}$  state. Note as well that the stimulated transitions are also fully allowed. While this technique is not widely used to study atomic transitions (or the chemistry of novel excited states of atoms), it is used to study novel states of molecules to great advantage. See page 768 in the text.



- 18.29 If the internal energy of a photon gas is  $U = \eta VT^4$  and if  $G = -U/3 = -\eta VT^4/3$ , then the thermodynamic relation  $S = -(\partial G/\partial T)$  tells us that  $S = 4\eta VT^3/3$ . An adiabatic reversible process is one that occurs at constant entropy, and thus  $S =$  a constant means  $VT^3 =$  a constant. Finally, the equation of state of the ideal photon gas follows from  $P = -(\partial G/\partial V) = \eta T^4/3$  or  $PV = \eta VT^4/3 = U/3$ .